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Synthesis, Characterization and Photocatalytic Activity of Calcareous/TiO_2 Nanocomposites under UV Light Irradiation using Methylene Blue Dye

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ABSTRACT

Titanium dioxide (TiO_2) occurs in three basic modification anatase, rutile and brookite. Anatase is widely studied due to its very good photocatalytic properties, which may be used in additives to paints and construction materials, degradation of organic pollutants in air and water etc.,. In the present work, the synthesis, characterization and photocatalytic activity of calcareous/TiO_2 nanocomposites on the removal of methylene blue dye were carried out by using solvothermal method. Synthesized nanocomposites was characterized by using XRD, SEM, EDAX and UV-Vis absorption spectroscopy. The XRD pattern reveals the course of composites formation and calcareous/TiO_2 nanocomposites containing anatase phase of TiO_2 were found. The higher photocatalytic activity was obtained in anatase phase of TiO_2 than rutile. It is concluded that the higher photocatalytic activity in anatase is due to parameters like band gap, number of hydroxyl groups, surface area and porosity of catalyst. The spherical morphology of calcareous/TiO_2 nanocomposites was observed in SEM analysis. The photocatalytic efficiency of various operational parameters like concentration, time, catalyst loading and pH on methylene blue dye was also studied.

1. Introduction

Anatase has stronger antimicrobial and photocatalytic activity than rutile [1-3]. Clays, such as montmorillonite, rectorite and kaolinite have attracted much attention in recent years for their applicability, in the waste water treatment. These natural materials possess layer structures, large surface areas, and high cation exchange capacities and can adsorb organic substances either on their external surfaces or within their interlaminar spaces by interaction or substitution. It has been reported that dispersion TiO_2 particles into layered clays can improve catalyst performance because such composites structures can stabilize TiO_2 crystals for access by various molecules [4, 5]. Enhancement in material research significantly supports application of titanium dioxide in the field of photocatalyitc materials for potential applications in civil engineering. The important applications of titanium dioxide are on photocatalysis in the field of building materials are self-cleaning and self-disinfecting. The advantage of using solar light and rainwater as driving force has opened as new domain for environmentally friendly building materials [6]. Among various oxide semiconductor photocatalyst, TiO_2 is an important photocatalyst due to its strong oxidizing power, non – toxicity and long – term photostability. Specific applications TiO_2 crystalline particles are determined by chemical, structure and physical properties. TiO_2 exists in three different crystalline phases, where the anatase and brokite are metastable states. Effluents containing dyes often create severe environmental pollutions because of their direct disposal into the nearby water bodies [7]. Most of the synthetic textile dyes are azo compounds, that is they contain N=N linkage in their structure. About 15% of the dyes are lost in waste water during dyeing operation. This affects the esthetic merit of surface water and reduces light penetration, hampering aquatic lives and hindering photosynthesis. Moreover, some dyes are either toxic or mutagenic and carcinogenic [8]. Titania is a well-known material in photocatalysis. As a semiconductor with wide band energy and non-toxicity, it is widely used for photocatalytic decomposition of various organic compounds in waste water treatment [9-11]. Ultrafine powders of TiO_2 have large specific surface areas and are expected to have good catalytic activities since reactions take place on the TiO_2 surface. However, the use of titania in bulk from suffers from some practical problem, such as catalyst agglomeration and difficult recovery, which results ineffective application of the catalyst. This problem can be solved in part if TiO_2 is immobilized on the inert supported materials without loss of activity. Thus, various kinds of supports like silica, alumina, activated carbon, zeolite and clay [12-15] are most widely used to immobilize the catalyst. Among them, clay and clay based matrix are promising materials because they are chemically inert, resistant to deterioration and commercially available in larger quantities [16-18]. The existence of organic dyes in wastewater is not desired from the point of view of health and also esthetics. Organic dyes, owing to their non-biodegradebility, toxicity and carcinogenic nature, constitute a major threat to the ecosystem. It is reported that several physical, chemical and biological methods are presently available for the treatment of wastewater, but each of these conventional methods has disadvantages [19, 20]. Heterogeneous photocatalysis is an attractive and highly efficient method for the degradation of toxic chemicals in industrial wastewater [21, 22].

2. Experimental Methods

Clay – water dispersion (1% w/w) was stirred for 2 hours. An aliquot of TiO_2 sol was added to the dispersion, to obtain a final TiO_2 content of 70% w/w. The slurry was stirred for 24 hours. The resulting dispersion was centrifuged at 3800 rpm for 10 minutes. The solid phase was washed with ultrapure water followed by triplicate centrifugation. The resulting clay – TiO_2 composite was dispersed in 1:1 water: ethanol solution, prior to hydrothermal treatment in an autoclave at 180 °C for 5 hours. The product was centrifuged once again at 3800 rpm for 15 minutes, and oven dried at 60 °C for 3 hours.

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2.1 Instrumental Characterizations

XRD measurements are performed using a Philips diffractometer of 'X' pert company with monochromatized Cu Kα (λ=1.54060 Å) radiation. For determination of crystallite size, Scherrer's analysis on XRD is commonly used. A double beam UV-Vis (Jascow – 500) spectrophotometer with 1 mm optical path length quart cells was used for all absorbance measurement in the range of 200 nm – 800 nm. SEM image was obtained by using HITACHI-S-3400H model.

2.2 Photocatalytic Activity

The prepared methylene blue dye solutions are taken in UV multilamp photoreactor tube. The required amount (0.020 g) of synthesized material was added to the above dye solution. Before irradiation the dye solutions were kept under dark condition for 30 min to obtain adsorption-desorption equilibrium. Then it kept inside UV multilamp photoreactor for 80 min. The collected suspension was centrifuged and filtered before the UV-visible absorption measurements. The degradation rate of dye was estimated by the following equation,

$$\text{Percentage removal (\%R)} = [C_i - C_f/C_i]\times 100 \quad (1)$$

where C_i & C_f is the initial & final concentration of dye (ppm) at a given time.

3. Results and Discussion

3.1 X-Ray Diffraction (XRD) Analysis

In order to determine the size and to study the structural properties of the synthesized nanocomposites of TiO_2, the powder XRD analysis was performed, which is shown in Fig. 1. It can be clearly observed that the diffraction peaks appear in the pattern corresponding to the anatase phase of TiO_2. The spectra showed crystalline nature with 2θ peaks lying at 2θ=25.25° (101), 2θ=37.8° (004), 2θ=47.9° (200), 2θ =53.59° (105) and the average crystallite size has been calculated from the recorded XRD patterns using well known Scherrer's equation D=0.89λ/βcosθ of TiO_2 nanocomposites has been found to be 16 nm respectively. The similar result was reported by Daimei Chen *et al.* [23].

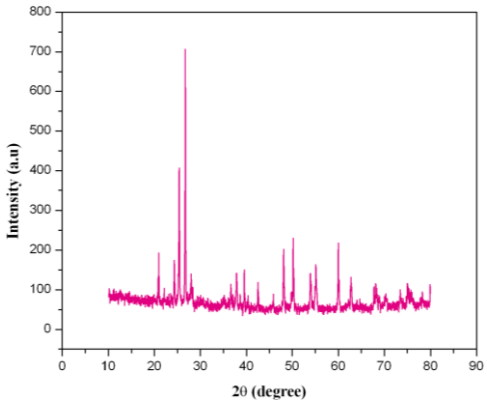

Fig. 1 XRD pattern of Calcareous/TiO_2 nanocomposites

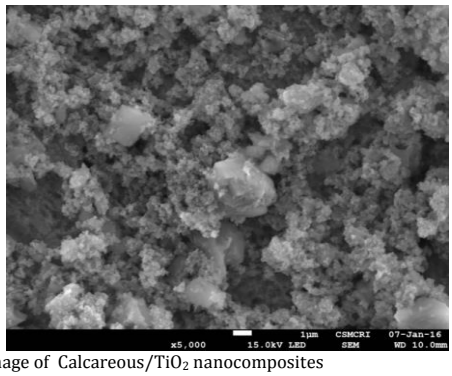

Fig. 2 SEM image of Calcareous/TiO_2 nanocomposites

3.2 SEM with EDAX Analysis

Scanning electron microscope (SEM) was used for the morphological study of synthesized nanocomposites of TiO_2. Fig. 2 shows the SEM images of the as prepared TiO_2 nanocomposites. The TiO_2 nanocomposites formed were highly agglomerated. The spherical shaped particles with clumped distributions are visible through the SEM analysis. The result was well matched with Suresh *et al.* [24]. The elemental presences are given in Fig. 3.

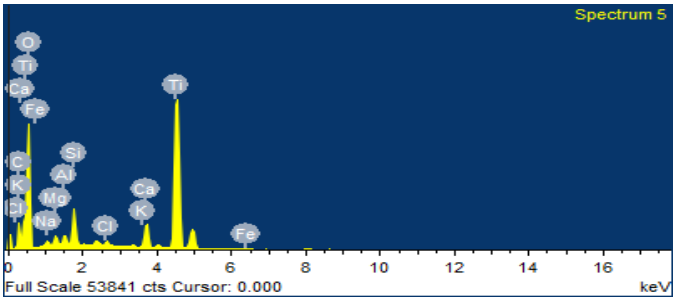

Fig. 3 EDAX spectrum of calcareous/TiO_2 nanocomposites

3.3 UV-Vis Absorption Spectroscopy

The UV visible spectrum indicates that the absorption edge shifted towards lower wavelength for calcareous/TiO_2 nanocomposites. This is clearly indicated an increase in the band gap energy of calcareous/TiO_2 nanocomposites. This is shown in Fig. 4. The band gap energy can be estimated from the following equation [25],

$$\alpha = \frac{k(h\nu - E_g)^{n/2}}{h\nu} \quad (2)$$

where, $h\nu$ is the photon energy, A and n are constants. While n is 2 for direct energy gap and ½ for an indirect energy gap.

Plots of $(\alpha h\nu)^2$ versus photon energy (hν) for calcareous/TiO_2 nanocomposites is given in Fig. 5. The band gap energy is estimated from the intercept of the tangents of the plot is 3.5 eV. This showed that the blue shifted when compared with the bulk TiO_2 (3.2 eV). The blue shift might be caused by nanosize effect and structural defect of nanomaterials.

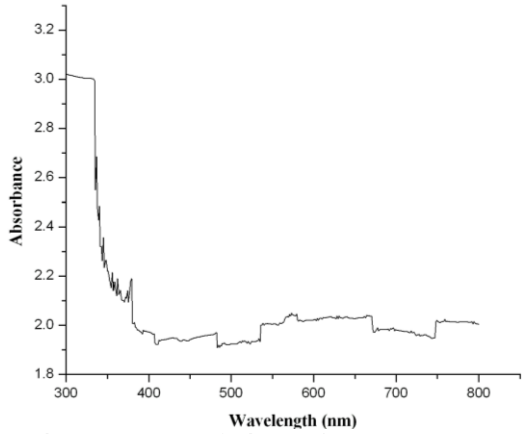

Fig. 4 UV-vis absorption spectrum of calcareous/TiO_2 nanocomposites

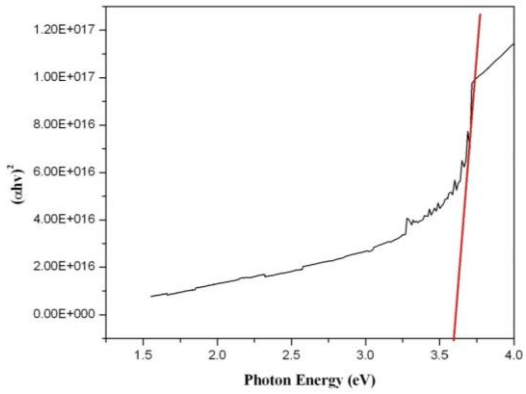

Fig. 5 Band gap energy of calcareous/TiO_2 nanocomposites

3.4 Photocatalytic Activity of MB Dye

3.4.1 Contact Time

It is clearly seen that the percentage degradation increases with increasing irradiation time and is 88.3% degradation at 30 minutes using calcareous/TiO_2 nanocomposites. This may be due to with increase in

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irradiation time dye molecules and catalyst loading have a enough time to take part in photocatalytic degradation of MB dye process and hence percentage of degradation increases. The trend is shown in Fig. 6. The results of experiments showed that the photocatalytic degradation of MB dye obey apparently pseudo first order kinetics and the rate expression is given by the following equation,

$$In(C_0/Ct)=Kt \quad (3)$$

where, C_o=initial concentration of dye solution; Ct=final concentration of dye solution in various time interval.

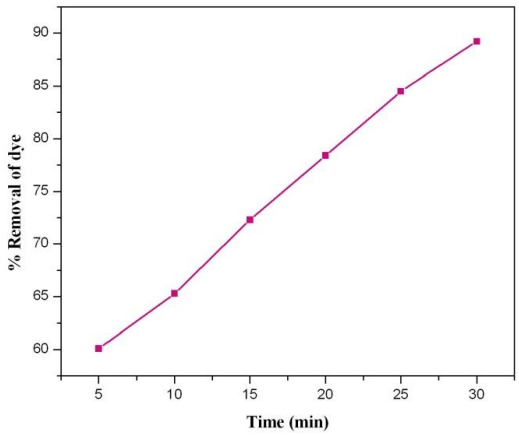

Fig. 6 Effect of contact time

3.4.2 Effect of Dosage

The amount of catalyst loading is one of the main parameters for the degradation studies. The results for the dye degradation using various amounts of TiO_2 (0.10 mg-0.26 mg) are shown in Fig. 7. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of dye. The results showed that when catalyst dosage was increased from 10-26 mg, the decolourization increases from 41% to 88.2%. The increase in degradation rate with increase in the catalyst loading is due to increase in total active surface area i.e. availability of more active sites on catalyst surface. However, it increases significantly upon addition of TiO_2 due to the production of higher amount of hydroxyl radical through the interaction of UV with TiO_2. But above 20 mg of TiO_2 the colour removal efficiency significantly increases due to increase of formation of hydroxyl radicals. With increasing catalyst loading the number of active sites increases, but the penetration of UV light decreases due to shielding effect. It should also be noted that the optimum value of catalyst loading is strongly depended on the type and initial concentration of the pollutant and the operating conditions of the photoreactor.

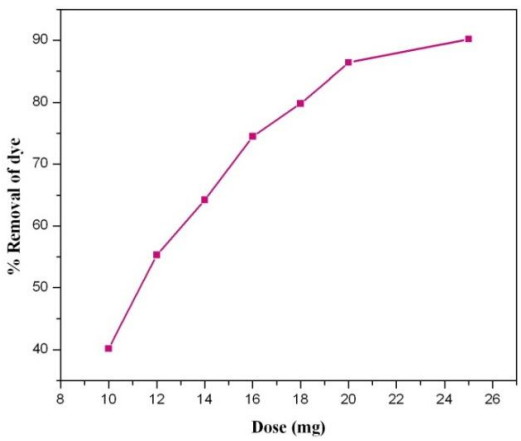

Fig. 7 Effect of dosage on MB removal

3.4.3 Effect of Initial Dye Concentration

The effect of initial concentration of dyes on the percentage degradation was studied by varying the initial concentration from 10 ppm to 60 ppm in the case of MB dye. That percentage degradation decreases with increasing initial concentration of the dye. The possible explanation for this behavior is that as initial concentration of the dye increases, the path length of photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photons absorption by the catalyst in lower concentration. This suggests that as the initial concentration of the dye increases the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of TiO_2 is also constant. So the relative number of free radicals attacking the dye molecules decreases with increasing amount of the catalyst. The major portion of degradation occur in the region near to the irradiated side, since the irradiation intensity in this region is much higher than that at the other side. Hence, at higher concentration, degradation decreases at sufficiently longer distances from the light source or reaction zone due to the retardation of penetration of light .Thus, the rate of degradation decreases with increase in concentration of dyes which is observed in Fig. 8.

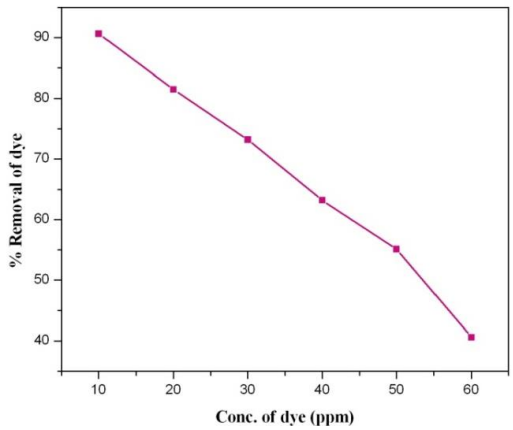

Fig. 8 Effect of initial dye concentration

3.4.4 Effect of pH

The waste water from textile industries usually has a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH. Thus the pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Photodegradation process was examined at pH values ranging from 2 to 10 for the MB dye. In all the experiments pH was adjusted by adding appropriate amount of 0.02 N H_2SO_4 or 0.2 N NaOH solution. The effect of pH on the degradation is shown in the Fig. 9. Further, the generation of hydroxyl radicals is also a function of pH. The pH values increases from 3 to 11 for MB dye. The zero point charge for TiO_2 is 6.25. In MB dye pH increases from 3 to 11 higher percentage removal (at basic condition) was occurred. In this condition the surface of the catalyst will become negatively charged. So MB dye easily attracted by the catalyst [26-28].

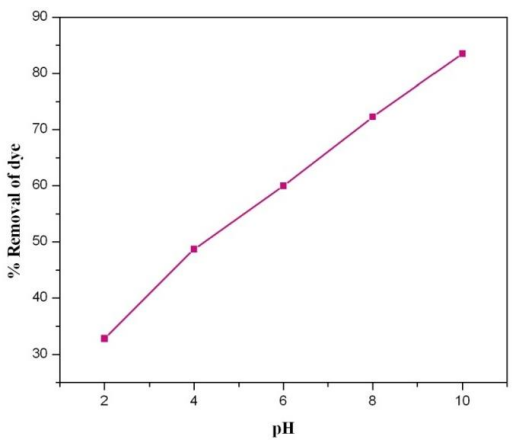

Fig. 9 Effect of pH on removal of MB

4. Conclusion

The calcareous/TiO_2 nanocomposites have been successfully synthesized by using solvothermal method. The prepared nanocomposites were characterized by using various analytical tools like XRD, SEM with EDAX, UV-Vis absorption spectrum. The XRD result reveals that the presence of anatase phase of TiO_2. The synthesized nanocomposites size and morphology of the sample were characterized by SEM with EDAX. SEM proved the spherical shape and well dispersed on the clay surface. The band gap energy of this nanocomposites is 3.4 eV, which is larger than the

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value of 3.2 eV for bulk TiO_2. The initial rate of photodecolorization increased with increase in catalyst dose upto an optimum loading. Further increased in catalyst loading showed no effect. As the initial concentration of dyes was increased, the rate of decolorization was decreased for MB dye. In MB dye pH increases from 3 to 11 higher percentages removal (at basic condition) was occurred. In this condition the surface of the catalyst will become negatively charged and hence the MB dye is easily removed the catalyst.

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